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The Final Proceedings for Irish Atomistic Simulators' Meeting, 17 December 2001 - 18 December 2001. The following topics were covered during this conference: computational materials science, electronic structure theory, atomic scale simulation, multi-scale modeling, nanotechnology simulation

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+44 (0)20 7514 3154

6th IRISH ATOMISTIC SIMULATION MEETING
UNIVERSITY COLLEGE CORK
DECEMBER 17-18, 2001

CONFERENCE SCHEDULE

Venue: All talks will be held in National Microelectronics Research Centre, Main Conference Room, Lee Maltings, Prospect Row, Cork.

Monday, December 17

2:30pm
Simon Elliott, NMRC   Simulating the growth of high-k dielectric films

2:50pm
Graeme Watson, TCD Chemistry Density Functional Theory study of the absorption and diffusion of hydrogen on the [111] surfaces of Ni, Pd, and Pt

3:10pm
Sorcha Healy, UCC Physics   Ultrafast Optical Excitation of Phonons in Tellurium

3:30pm
N. P. Konstantinides, TCD Physics Perturbation theory for strongly frustrated finite spin systems

3:50–4:20pm   **coffee break**

4:20pm
Eoin O'Reilly, NMRC   GaInNAs is good for you!

4:40pm
Martin Peters, TCD Chemistry DNA Triplexes, a study of their Hydrogen bonds

5:00pm
G. Zheng, TCD Physics   First principles simulations of exchange coupling in La_2CuO_4: configuration interaction calculations and the coupling mechanism

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5:20pm	
Arnaud Marmier, QUB ASG	Dynamics and free energy of Alumina surfaces, semi-empirical and DFT calculations
5:40pm	
M. NiCastro, TCD Physics	Exchange coupling in $CaMnO_3$ and $LaMnO_3$: UHF and CI calculations

8:00pm — Conference Dinner at Proby's Bistro, Proby's Quay

Tuesday, December 18

9:00am	
S. Galamić-Mulaomerović, TCD Physics	Dielectric matrix calculation and dielectric response eigenfunctions for silicon and solid argon
9:20am	
David Prendergast, UCC Physics	Energy optimization of correlated many-electron wavefunctions
9:40am	
Sasha Lozovoi, QUB ASG	Ab initio calculation of charged metallic surfaces
10:00am	
Ciara Bergin, TCD Chemistry	Molecular dynamics simulation of an alkanoate monolayer on water
10:20am	
Jorge Kohanoff, QUB ASG	Ferroelectricity and isotope effects in H-bonded solids: KDP and beyond
10:40–11:20am	**coffee break**
11:10am	
Matthew Manktelow, TCD Chemistry	An Exploration of Binary Information Patterns in the Genetic Code
11:30am	
Donal Mac Kernan, CECAM	Surface-Hopping Dynamics of a Spin-Boson System
11:50am	
Christof Hanke, QUB ASG	Water-mixtures of ionic-liquids
12:10am	
A. Rowan, TCD Physics	Response function calculation for MgB_2

Affiliations of Speakers:

Ciara Bergin	Department of Chemistry, Trinity College, Dublin.
Simon Elliott	Materials Modelling Group, National Microelectronics Research Centre, UCC, Cork.
Christof Hanke	Atomistic Simulation Group, Queens University, Belfast.
Sorcha Healy	Department of Physics, University College, Cork.
S. Galamić-Mulaomerović	Department of Physics, Trinity College, Dublin.
Jorge Kohanoff	Atomistic Simulation Group, Queens University, Belfast.
N. P. Konstantinides	Department of Physics, Trinity College, Dublin.
Sasha Lozovoi	Atomistic Simulation Group, Queens University, Belfast.
Arnaud Marmier	Atomistic Simulation Group, Queens University, Belfast.
Donal Mac Kernan	Centre Europeen de Calcul Atomique et Moleculaire, Lyon, France.
Matthew Manktelow	Department of Chemistry, Trinity College, Dublin.
M. NiCastro	Department of Physics, Trinity College, Dublin.
Eoin O'Reilly	National Microelectronics Research Centre, UCC, Cork.
Martin Peters	Department of Chemistry, Trinity College, Dublin.
David Prendergast	Department of Physics, University College, Cork.
A. Rowan	Department of Physics, Trinity College, Dublin.
Graeme Watson	Department of Chemistry, Trinity College, Dublin.
G. Zheng	Department of Physics, Trinity College, Dublin.

ABSTRACTS OF PRESENTATIONS

Simulating the growth of high-k dielectric films

Simon Elliott
Materials Modelling Group, National Microelectronics Research Centre, UCC, Cork

Conventional MOS transistors using SiO_2 gate oxides are still being scaled down, but face a severe restriction on minimum device size: they are limited by the high field gradients and large tunnelling currents across the very thin gate layer of SiO_2. Oxides such as HFO_2, ZrO_2 and Al_2O_3 have high dielectric constants (k) and are being proposed to replace SiO_2, thereby promising comparable insulating performance but with thicker gate layers. We report on a project which aims to fill the gap in understanding for the behaviour of these new oxides, by multi-scale simulation of the deposition process.

Density Functional Theory study of the absorption and diffusion of hydrogen on the [111] surfaces of Ni, Pd, and Pt

Graeme Watson
Department of Chemistry, Trinity College, Dublin.

We present gradient corrected density functional theory calculations on the adsorption and thermally activated diffusion pathways of hydrogen on the (111) surfaces of Ni, Pd and Pt. We find that the variation of the adsorption energy as a function of adsorption site shows considerable differences between the three metals. For Ni and Pd the adsorption energies vary as a function of hydrogen co-ordination, with the 3-fold hollow sites the most stable and the 1-fold atop site considerably less stable. On Pt the adsorption energies for all the sites are similar, indicating that diffusion across the surface will be faster on Pt than on Ni or Pd. The activation energies for diffusion have been calculated, with that for Pt (2-3 kJ mol^{-1}) considerably smaller than for Ni or Pd (13 kJ mol^{-1}). This is related to the experimental data on hydrogenation activity and is a possible contributing factor to the differences observed in reactivity.

Ultrafast Optical Excitation of Phonons in Tellurium

Sorcha Healy and Stephen Fahy
Department of Physics, University College Cork

The coupled dynamics of photo-excited carriers and the A_1 and A_2 phonons are simulated for ultra-fast optical pump-probe experiments on tellurium. Carrier diffusion and drift due to electron-phonon coupling to the A_1 phonon are considered. Different diffusion rates

for electrons and holes generate strong electric fields near the surface of the photoexcited material on a ps time-scale, and these electric fields couple to the infra-red active A_2 phonon. We examine the expected damping of the A_1 phonon for very large fluence of the pump pulse and find that it differs substanially from that observed in experiment.

Perturbation theory for strongly frustrated finite spin systems

N. P. Konstantinidis
Department of Physics and Centre for Scientific Computation, Trinity College Dublin
D. Coffey
State University of New York at Buffalo, Amherst, USA

Degenerate perturbation theory in high orders is applied for a series of strongly frustrated magnetic clusters. An effective Hamiltonian for the low energy states is constructed as a power series in the perturbation parameter λ. The series converge asymptotically and are summed using Padé approximants, providing the low energy spectrum and the corresponding wavefunctions. The first class of systems investigated are "toy" Heisenberg models with connectivity similar to the one of molecules of C, known as fullerenes. The magnetic properties of these systems as functions of magnetic field depend strongly on the connectivity at the classical level, and this dependence is found to survive at the quantum level. Furthermore, the dependence of magnetization on the number of sites is reflected in the analytic structure of the ground state energies and wavefunctions as functions of λ. The second system studied is a model for the magnetic molecule V_{15}. The model includes a Heisenberg term, and magnetic anisotropy is included with a symmetry allowed Dzyaloshinskii-Moriya interaction. The properties of the model are calculated as functions of temperature and magnetic field. By comparing with data the parameters of the DM interaction are evaluated. The magnetic anisotropy term is found to be an intrinsic source of decoherence for moments induced by magnetic fields even at zero temperature.

DNA Triplexes, a study of their Hydrogen bonds

Martin Peters
Department of Chemistry, Trinity College, Dublin.

An *ab initio* study of novel DNA triplexes and prediction of their hydrogen bonding interactions using Bader's theory of 'Atoms in Molecules' is presented. We discuss how the lapacian of the electron density can characterise the triplexes interactions.

First principles simulations of exchange coupling in La_2CuO_4: configuration interaction calculations and the coupling mechanism

G. Zheng and C.H. Patterson
Department of Physics and Centre for Scientific Computation, Trinity College Dublin

The exchange constants of La_2CuO_4 have been investigated using localised orbital configuration interaction (CI) calculations on clusters. Exchange constants from ab initio calculations on clusters containing two and four Cu ions are compared to estimates for these quantities based on analysis of spin wave experiments. Calculations show that exchange interactions between the $d_{x^2-y^2}$ orbitals play a very important role in the exchange coupling of La_2CuO_4 and O to $d_{x^2-y^2}$ excitations have secondary importance in the La_2CuO_4 ground state. The coupling mechanism is discussed.

Dynamics and free energy of Alumina surfaces, semi-empirical and DFT calculations

Arnaud Marmier
Atomistic Simulation Group, Queen's University Belfast

We report an atomistic investigation of static and dynamic properties of the (0001) surface of alpha-alumina (Al_2O_3) at different temperatures. Lattice dynamics calculations are performed within the quasi harmonic approximation and with two parameterization of the shell model as well as with a DFT description. The simple models provide a convenient benchmark for testing the convergence of different dynamic related properties with respect to slab parameters (thickness, vacuum size) and to vibrational k-point sampling. The surface systematically undergoes an important relaxation, whose details are highly model dependent. The free energy is calculated for different sampling of the vibrational Brillouin zone. We show that it can already be excellently approximated with a simple 2 k-points sampling. The analysis of the mean square displacement of the atoms shows that the surface atoms are between 1.5 and 2 times more mobile than the their bulk counterparts. We do not find tracks of modes strongly localized on the surface Al atoms with the classical model. On the other hand, with the DFT model there is clearly such a mode. However, it is not strongly anharmonic and cannot account for the discrepancies between ab initio surface relaxations and experimentally determined ones. This makes the alternative explanation of surface impurities more likely, but so far the experimentalists have failed to detect any.

Exchange coupling in $CaMnO_3$ and $LaMnO_3$: UHF and CI calculations

M. Nicastro and C.H. Patterson
Department of Physics and Centre for Scientific Computation, Trinity College Dublin

The equilibrium structure and the exchange coupling mechanism in $CaMnO_3$ and $LaMnO_3$ have been investigated using UHF calculations on the bulk crystal and CI calculations on clusters representing the two compounds. In the case of $LaMnO_3$ a series of UHF calculations on a cubic idealized structure shows that independent orbital ordering and exchange terms contribute to the Hamiltonian. For both systems CI calculations reveal a strong dependence of exchange constants on the Madelung potential of the cluster and on the population of Mn d e_g orbitals. Analysis of the CI wave functions shows which exchange processes are important in the exchange coupling mechanism. Predicted exchange constants are in reasonable agreement with experimental values estimated from the Neél temperature.

Dielectric matrix calculation and dielectric response eigenfunctions for silicon and solid argon

S. Galamić-Mulaomerović and C. H. Patterson
Department of Physics and Centre for Scientific Computation, Trinity College Dublin

The symmetrised dielectric matrix (DM) has been fully calculated for solid argon and silicon using Gaussian orbital basis sets. Calculation of the DM involves summation over both occupied and unoccupied states and special care has to be taken while constructing the basis set. The dependence of the DM elements on Gaussian orbital bases will be presented and compared with published data. The dynamical dielectric function and dielectric response function are calculated within the RPA for silicon and solid argon and compared to a full numerical calculation of these functions. The plasmon pole-model for the response function is used to obtain the plasmon dispersion inside the first Brillouin zone and results are compared with the fully numerical calculation.

Energy optimization of correlated many-electron wavefunctions

David Prendergast and Stephen Fahy
Department of Physics, University College Cork

In a new iterative variational Monte Carlo method, the total electronic energy is minimized with respect to a general expansion of the inhomogeneous electron correlation terms in a many-electron wave function for a periodic solid. The description of inhomogeneity in such systems represents a small percentage of the correlation energy, therefore determination of the optimal variational wave function parameters is extremely delicate. Our method, based on fitting energy fluctuations, is rapidly convergent and produces statistically well-determined parameters and correlation functions, even when a large number of parameters (approx. 3000) and electrons (approx. 200) are involved. Applications to the study of correlation factors in diamond and graphite are shown.

Ab initio calculation of charged metallic surfaces

Sasha Lozovoi
Atomistic Simulation Group, Queen's University Belfast

Various properties of metallic surfaces are known to be affected by the presence of external electrostatic fields (or equivalently, by appearance of surface charge). In addition, these inevitably arise in some experimental techniques such as STM, FIM, and electrochemistry. We shall describe a scheme to calculate the energies associated with charged surfaces such as they could be directly compared. We then demonstrate how the method works on example of the missing-row reconstruction of Au(110) and Pt(110) surfaces.

A molecular dynamics simulation of an alkanoate monolayer on water

Ciara Bergin
Department of Chemistry, Trinity College, Dublin.

The features associated with simulating an amphiphile layer on a water surface are described. A simulation of liquid water was first achieved so as to give satisfactory values of certain bulk properties, together with the establishment of a liquid-vacuum interface which disappeared at higher temperatures. Alkanoate anions were then sited with their hydrophilic regions (the polar COO group) below the liquid surface, and their alkyl chains directed into the vacuum, perpendicular to the interface. The all-trans conformations of the chains were approximately maintained, but showed departures with changing pressure and temperature.

Ferroelectricity and isotope effects in H-bonded solids: KDP and beyond

Jorge Kohanoff
Atomistic Simulation Group, Queen's University Belfast

Hydrogen-bonded molecular crystals normally undergo an order-disorder phase transition at temperatures around 100-200 K. This is a structural transition accompanied by a change in the dielectric properties of the material, like ferro or antiferroelectricity. The transition temperature is extremely sensitive to the isotopic substitution of H by D. This isotope effect has been explained in two ways: (1) the tunneling model postulating that the main ingredient is the correlated tunneling of the protons in an effective double-well potential, and (2) the geometric effect which is based on the modification of the geometry of the hydrogen bonds upon isotopic substitution. Both theories give results compatible with experimental data. We have thoroughly analysed the case of KPO_4H_2 (KDP) by means of first-principles calculations for global and (correlated) local moves of the protons. Our results indicate a predominance of the geometric effect, which is mainly connected to a modification of the lattice constants. The relevant moves involve not only protons, but

also the displacement of heavy atoms like P, a fact that is connected to the appearance of ferroelectricity. The transition disappears if sufficient pressure is applied. The order parameter (polarization), however, does not vanish at T_c, and the protons remain off-center in the H-bonds at a distance of 0.1 A from the middle of the bond. This result appears to be universal for the whole family. We observe this feature in our first-principles calculations for KDP, and use it to speculate about its universality.

An Exploration of Binary Information Patterns in the Genetic Code

Matthew Manktelow
Department of Chemistry, Trinity College, Dublin.

The universal genetic code employs the physical features of nucleotides to transmit information. We report the results of qualitative and quantitative analyses of these features where idealised binary patterns are compared with data derived from evolutionary substitution rates. The analysis offers some insight into the structure of the genetic code.

Surface-Hopping Dynamics of a Spin-Boson System

Donal Mac Kernan[†], Giovanni Ciccotti[†,*] and Raymond Kapral[†,‡]
[†]CECAM, Ecole Normale Superieure de Lyon, France
[*]INFM and Dipartimento di Fisica, Università "La Sapienza", Roma, Italy
[‡]Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Canada

In this talk the spin-boson model is solved within the framework of quantum-classical dynamics using our recently-developed surface-hopping scheme. The quantum-classical equation of motion is expressed in an adiabatic basis and its solution is constructed from an ensemble of trajectories which undergo non-adiabatic transitions and evolve coherently on the adiabatic surfaces. Details of the algorithm for the simulation of the dynamics are presented and the method of simple Monte Carlo sampling used to evaluate the expectation values of observables is discussed. For the spin-boson model the present implementation of quantum-classical dynamics is exact and the results of our surface-hopping simulations are in accord with previous numerically exact results for this model.

Water-mixtures of ionic-liquids

Christof Hanke
Atomistic Simulation Group, Queen's University Belfast

Hydrogen-bonded molecular crystals normally undergo an order-disorder phase Ionic liquids are basically molten salts, which are due to the size of the ions already liquid at

temperatures less than 100 C. Some of these liquids are vey hygroscopic and change their physical properties with increasing water content. In this talk, some of the properties of the ionic liquids 1,3-methylmethylimidazolium (mmim) / Cl and mmim / PF6 are discussed, both as neat liquids and with different water-contents.

Response function calculation for MgB_2

A. Rowan, S. Galamić-Mulaomerović and C. H. Patterson
Department of Physics and Centre for Scientific Computation, Trinity College Dublin

MgB_2 was recently discovered to be superconducting up to 40K. Its structure may be regarded as boron in layers with the graphite structure, which sandwich Mg ions. Eigenfunctions of the dielectric response function are used to analyse charge density response to an external potential in MgB_2 and to identify the charge density oscillation mode likely to be responsible for anomalously strong electron- phonon coupling in this material.